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**Photoinduced Orientation and Some of Its Photonic Consequences in  
Amorphous Azo-Containing Polymers**

**by**

**A. Natansohn and P. Rochon**

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PHOTOINDUCED ORIENTATION AND SOME OF ITS PHOTONIC  
CONSEQUENCES IN AMORPHOUS AZO-CONTAINING POLYMERS. A.  
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Photoinduced birefringence, surface gratings inscription and two-beam coupling properties are investigated on a series of amorphous high-Tg azo-containing polymers. For photoinduced birefringence, a neighboring group effect was observed, and dipolar interaction is demonstrated to be the main factor determining cooperative motion of side groups below Tg. Surface gratings can act as optical couplers into waveguides on the polymer films. Asymmetrical (photorefractive) and two-beam coupling due to multiwave mixing can be exploited for switching elements. In principle, a whole photonic device can be envisaged on a simple polymer film and obtained by optical inscription.

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# PHOTOINDUCED ORIENTATION AND SOME OF ITS PHOTONIC CONSEQUENCES IN AMORPHOUS AZO-CONTAINING POLYMERS

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Three different properties are of interest in the study of azo-containing polymers in our laboratory:

## Photoinduced Birefringence

In the process of photoinducing orientation in amorphous azo-containing polymers, we have identified a few structural factors affecting the level and the rate of inducing birefringence. The most interesting factor is a neighboring groups effect, which favors cooperative motion of azobenzene groups bound on the same polymer chain<sup>1-3</sup>. Since this effect is evidenced for the first time in amorphous polymers, we were interested in determining if the driving force was steric (as is the case in liquid crystalline polymers, where the rigid groups move in concert due mainly to their similar shape) or dipolar. A dipolar driving force would arise from the electric field of the neighboring rigid dipoles. Experimental evidence up to date strongly suggests that the driving force is dipolar. A rigid group of similar shape and polarity (a substituted phenyl benzoate ester, for example)<sup>3</sup> moves in concert with the azobenzene group when the latter is moved by polarized light. If the same group (same size, same shape) has a much smaller dipole moment ("non-substituted" phenyl benzoate)<sup>4</sup>, no cooperative motion is observed.

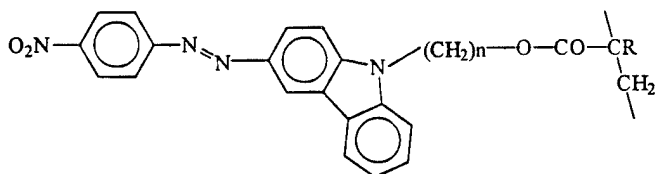
In-situ orientation studies performed by monitoring infrared dichroism while birefringence was being photoinduced, clearly show different motions of the azobenzene and of the phenyl benzoate groups<sup>5</sup>.

## Surface gratings

Deep periodic surface gratings can be inscribed on azobenzene-containing polymer films by interfering beams, thus giving the possibility for long-term holographic storage<sup>6,7</sup>. The mechanism of inscribing such gratings was proposed to be pressure-driven<sup>8</sup> and will be described in a separate paper in this symposium<sup>9</sup>.

## Two-beam coupling

A third property of some of the amorphous, high-T<sub>g</sub>, azobenzene-containing polymer films is the ability for two-beam coupling, symmetric and asymmetric. Symmetric two-beam coupling can be obtained after inscription of a volume grating on the film (exploiting differences in birefringence) or of a surface grating, as mentioned above. Either grating will diffract incoming beams and may produce gain or loss<sup>10</sup>. Asymmetric coupling can be obtained by exploiting the inherent photorefractive properties of at least some of these polymers<sup>10,11</sup>. An example of a class of polymers studied for its photorefractive properties is presented below:



These polymers contain the rigid polar azobenzene groups which can be poled in the presence of an electric field. Such an arrangement has electro-optic activity. The presence of the amino group provides

photoconductive properties, and in the case presented above, carbazole is a well-known photoconductive group in various polymer structures. When the combination of electro-optic activity and photoconductivity is present in a polymer, photorefractivity is a possibility<sup>12</sup>. Photorefractivity has been demonstrated in the visible ( $\lambda = 534$  nm) for thin films of the polymer with  $n = 2$  by performing asymmetric two-beam coupling<sup>10</sup>, which is a definitive test for photorefractivity<sup>13</sup>. By performing photoinduced poling with two interfering laser beams, birefringence gratings and surface gratings are also created in the polymer film, and the consequence is the appearance of two-beam coupling other than that produced by photorefractivity. Two-beam coupling due to multiwave mixing can be observed in the absence of an electric field. Thus, this third property is fairly complex and more research is required before it can be used for optical switching.

## Potential for devices

Stable birefringence can be locally induced and erased on a polymer film made of an azobenzene-containing polymer at a very high resolution. The birefringence can be used as a memory bit, or can be used for waveguide purposes. A "printed circuit" of waveguides can in principle be drawn on such a polymer film. At the points of incidence with a light beam coming from outside the film, the surface grating can be used to couple the external beam into and out of the polymer film. Such a surface grating can be obtained by exclusive optical means and its efficiency and direction of guiding are adjustable. Such a grating can also be erased, although local heating would be required for erasing. Finally, by local poling on films with photorefractive properties, or by exploiting symmetrical two-beam coupling, optical switches can be obtained. In principle, such an integrated circuit can be changed at will using only optical means.

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